



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



Publication number: **0 171 758 B1**

12

## EUROPEAN PATENT SPECIFICATION

45 Date of publication of patent specification: 16.09.92 51 Int. Cl.5: B01J 39/18

21 Application number: 85109974.7

22 Date of filing: 08.08.85

54 A process for preparing partially strong-acid cation-exchange resins in acid form.

30 Priority: 13.08.84 US 639980

43 Date of publication of application:  
19.02.86 Bulletin 86/08

45 Publication of the grant of the patent:  
16.09.92 Bulletin 92/38

84 Designated Contracting States:  
CH DE FR GB IT LI NL

56 References cited:  
GB-A- 1 183 564  
US-A- 3 760 006

PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 6, no. 19, 03.02.82, page 89 C 90

73 Proprietor: THE DOW CHEMICAL COMPANY  
2030 Dow Center Abbott Road P.O. Box 1967  
Midland Michigan 48640-1967(US)

72 Inventor: Fazio, Michael J.  
4617 Forestview Drive  
Midland Michigan 48640(US)

74 Representative: Sternagel, Hans-Günther, Dr.  
et al  
Patentanwälte Dr. Michael Hann Dr. H.-G.  
Sternagel Sander Ave 30  
W-5060 Bergisch Gladbach 2(DE)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

## Description

The present invention is directed to the preparation of partially-neutralized cation-exchange resins.

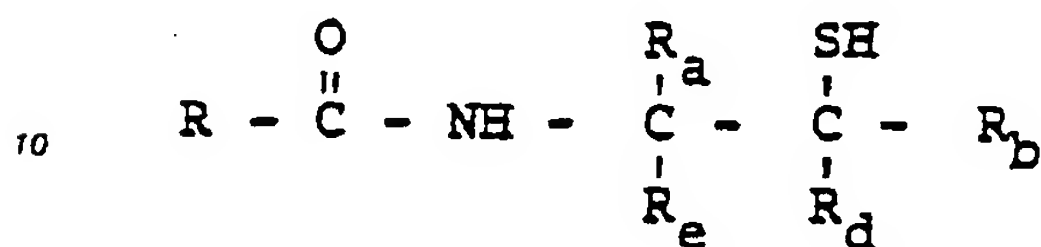
Ion-exchange resins frequently are employed as catalysts in the preparation of bisphenols from phenol and carbonyl compounds. For example, US-A-3,394,089 and GB-A-1183564 teach the use of a strong-acid cation-exchange resin partially neutralized with a C<sub>1</sub>-C<sub>4</sub> alkyl mercaptoamine such as 2-mercaptoethylamine (2-aminoethanethiol). Similarly, US-A-3,760,006 teaches that the modification of an insoluble strong-acid cation-exchange in acid form by partial neutralization with a thiazolidine yields an improved catalyst for the preparation of bisphenols. The latter patent teaches that the thiazolidines easily may be prepared by the reaction of a ketone or aldehyde, H<sub>2</sub>S, and an aziridine compound. In addition, it is known to prepare the mercaptoamines of the former patent from H<sub>2</sub>S and an aziridine, such as ethyleneimine. See, e.g., US-A-3,944,561 at column 2.

The partially neutralized ion-exchange resin catalysts are useful in the commercial production of bisphenols, especially bisphenol A. Unfortunately, current processes for producing the catalysts described hereinabove employ aziridine compounds which are somewhat hazardous. For example, ethyleneimine is described in The Condensed Chemical Dictionary (9th Edition) at page 361 as being highly toxic and corrosive; a dangerous fire and explosion hazard; and a known carcinogen. In view of these hazards, it would be very desirable to prepare said catalysts using a process which would not require the costly and hazardous aziridine compounds.

The present invention is a process for preparing an insoluble strong-acid cation-exchange resin in acid form modified by the partial neutralization of its cation-exchange capacity with an aminoalkanethiol characterized by contacting the cation-exchange resin with an N-(2-mercaptoalkyl)amide in the presence of water under reaction conditions sufficient to produce the modified cation-exchange resin. The partially neutralized resin can be treated further by contacting it with an aldehyde or ketone under reaction conditions sufficient to convert the aminoalkanethiol moieties to thiazolidine moieties. The method of the present invention, which employs an amide, is economically advantageous and is less hazardous than the known methods which employ aziridine compounds.

The N-(2-mercaptoalkyl)amide can be prepared by known methods, such as that taught in US-A-4,086,274. The method of that patent employs an oxazoline as a starting material. Thus, by using the relatively less expensive and less hazardous ox-

azolines as starting material precursors, the present invention advantageously eliminates the use of the costly, hazardous aziridines. Preferred N-(2-mercaptoalkyl)amides are represented generally by the formula:



wherein R, R<sub>a</sub>, R<sub>b</sub>, R<sub>d</sub>, and R<sub>e</sub> are independently H, alkyl or aryl. Preferably, R is alkyl of from 1 to 4 carbon atoms. Most preferably, R is ethyl or methyl and R<sub>a</sub>, R<sub>b</sub>, R<sub>d</sub>, and R<sub>e</sub> are H. The N-(2-mercaptoalkyl)amide is employed in an amount sufficient to neutralize the desired percentage of the strong-acid moieties of the cation-exchange resin. Typically, about a molar equivalent of N-(2-mercaptoalkyl)amide is employed per equivalent of hydrogen ions to be neutralized.

The process of the present invention can be employed to modify any insoluble strong-acid cation-exchange polymer. Examples of suitable polymers include perfluorinated sulfonic acid resins, strong-acid resins prepared by phosphonation of styrene-divinyl-benzene resins, and polymers such as those disclosed in US-A-4,303,551 and 4,330,654. Preferred polymers include aromatic sulfonic acid resins having a cation-exchange capacity of at least 0.5 and advantageously 2.0 or more meg/g dry weight. Commercial strong-acid resins prepared by the sulfonation of a styrene-divinyl-benzene resin, as described for example, by Bodamer in US-A-2,597,438, by Wheaton and Harrington in US-A-2,642,417 or by Bortnick in US-A-3,037,052, are most satisfactory. Commercial sulfonic acid resins which normally have an exchange capacity of 4.2-5.2 meg/g dry weight, make superior resin catalysts after partial neutralization.

The water employed in the process of the present invention serves as a solvent and serves to convert the N-(2-mercaptoalkyl)amide to the corresponding aminoalkanethiol. Water is employed in an amount sufficient to convert the amide to the corresponding aminoalkanethiol. Typically, from 0.5 to 3 volumes of water are employed per volume of resin beads, including void space. Preferably, water and beads are employed in equal volumes. The hydrolysis is substantially quantitative.

The neutralization of the polymer using the N-(2-mercaptoalkyl)amide can be conducted at any combination of temperature and pressure at which the neutralization can proceed and at which the polymer is stable. Preferably, the neutralization temperature is from 80° C to 110° C. More prefer-

ably, the neutralization is conducted at reflux temperature.

The extent of the neutralization of the catalyst may vary widely. The resin can be neutralized to any degree which improves the selectivity to the p, p'-bisphenol A isomer versus other isomers. Preferably, from 5 to 80 mole percent of the strong-acid groups of the cation-exchange resin are neutralized, with the neutralization of 15 to 40 mole percent of the strong-acid groups being preferred. Particularly effective catalysts are obtained by neutralizing a sulfonated aromatic resin having an initial exchange capacity of 4.5 to 5.2 meg/g dry weight in acid form giving a modified resin having a capacity of 3.6 to 4.4 meg/g dry weight in acid form. The degree of neutralization is readily verified by measuring via conventional methods, such as titration using NaOH, the ion-exchange capacity of the resin before and after partial neutralization. For a more detailed description of a typical catalyst which may be produced by the neutralization process of the present invention as described hereinabove see U.S. Patent 3,394,089.

The catalyst produced by the method described hereinabove may be contacted with an aldehyde or a ketone to convert the aminoalkanethiol neutralizing moieties to thiazolidine moieties. Thus, this additional step can produce a catalyst such as, for example, those described in US-A-3,634,341 and 3,760,006. Conversion of the aminoalkanethiol-bearing catalyst to the thiazolidine-bearing catalyst is carried out at any combination of temperature and pressure at which the cyclization occurs and at which the polymer is stable. Preferably, the cyclization is performed at a temperature of from 25°C to 50°C. The cyclization can employ any aldehyde or ketone which will cyclize the aminoalkanethiol moiety. Examples of typical aldehydes and ketones include cyclohexanone, methyl ethyl ketone, benzaldehyde, and methyl isobutyl ketone. Acetone is the preferred ketone. The aldehyde or ketone typically is employed in an amount sufficient to cyclize at least some of the aminoalkanethiol moieties of the neutralized catalyst. Preferably, at least 1 mole of aldehyde or ketone is employed per mole of aminoalkanethiol moiety. Excess aldehyde or ketone can be employed as a solvent for the cyclization.

The partially neutralized cation-exchange resin is an effective catalyst for the preparation of bisphenols using known techniques.

The following examples are given to illustrate the invention and should not be construed as limiting its scope. All parts and percentages are by weight unless otherwise indicated.

#### Example 1

A strong-acid cation-exchange resin (200 ml) available from The Dow Chemical Company under the trademark DOWEX® 50WX4, having a cation-exchange capacity of approximately 1.24 meg/H<sup>+</sup>/ml (5.17 meg/g dry weight), and 200 ml of deionized water are charged into a round-bottom glass flask having a volume of approximately 1 liter. The flask is purged with nitrogen. Then, 6.7 g of N-(2-mercaptoethyl)propionamide are added to the pot with stirring and the slurry is heated to reflux temperature, which is approximately 100°C. Six hours later the reaction mixture is cooled to room temperature and is filtered. The resin is then slurried with 200 ml of water and is filtered. This slurry and filter cycle is repeated four additional times. Analysis of the resin by titration with sodium hydroxide shows that 20 percent of the acid is neutralized with mercaptoethylamine.

#### Example 2

The procedure of Example 1 is repeated except that the resin employed has a cation-exchange capacity of approximately 1.27 meg/H<sup>+</sup>/ml (5.12 meg/g dry weight), and 11.1 g of the amide are charged into the slurry. Analysis of the isolated resin indicates that 34 percent of the acid is neutralized with mercaptoethylamine.

#### Example 3

Water (10 ml), DOWEX® 50WX4 (10 ml) and 1 ml of N-(2-mercaptoethyl)propionamide are slurried in a round-bottom glass flask and heated to reflux temperature under a blanket of nitrogen. Five hours later, the mixture is cooled to room temperature and filtered. The resin is then washed with 50 ml of water and then with 50 ml of acetone. The resin is then slurried in 25 ml of acetone at room temperature. The resin is allowed to stand in the acetone for 18 hours, and is then filtered.

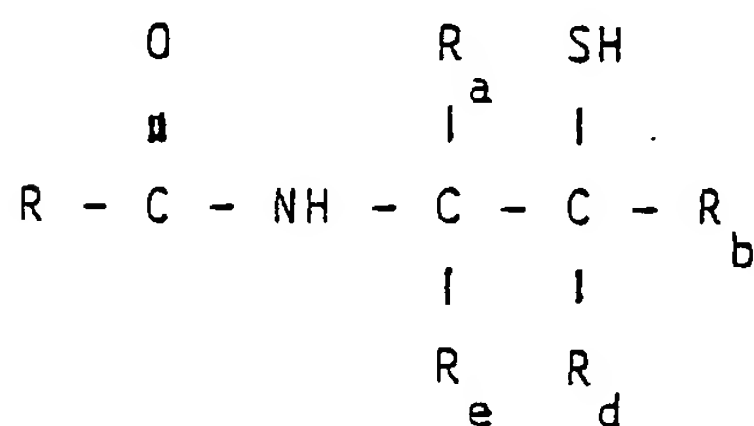
The formation of dimethylthiazolidine is verified by treating the resin with aqueous sodium hydroxide and extracting the aqueous phase with methylene chloride. The solvent is then removed from the organic phase at reduced pressure using a rotary evaporator. The residue is analyzed by H<sup>1</sup>-NMR. The spectral data is consistent with that of dimethylthiazolidine.

#### Claims

1. A process for preparing an insoluble strong acid cation-exchange resin in acid form modified by the partial neutralization of its cation-exchange capacity with an aminoalkanethiol characterized by contacting the cation-exchange resin with an

N-(2-mercaptoalkyl)amide in the presence of water at a temperature of from 80°C to 110°C under reaction conditions sufficient to produce the modified cation-exchange resin.

2. The process of Claim 1 characterized by employing a N-(2-mercaptoalkyl)amide having the formula:



wherein R, R<sub>a</sub>, R<sub>b</sub>, R<sub>d</sub>, and R<sub>e</sub> are independently H, alkyl or aryl.

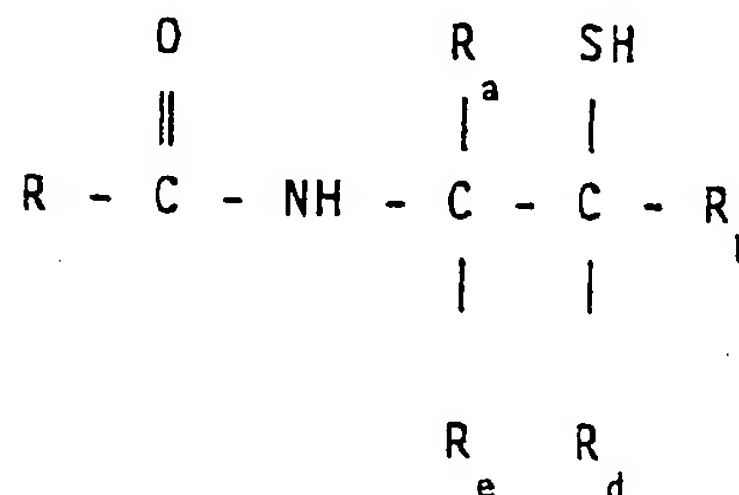
3. The process of Claim 2 characterized in that R is an alkyl group having from 1 to 4 carbon atoms.
4. The process of Claim 3 characterized in that R is methyl or ethyl, and R<sub>a</sub>, R<sub>b</sub>, R<sub>d</sub>, and R<sub>e</sub> are H.
5. The process of Claim 1 characterized by the additional step of contacting the partially neutralized resin with an aldehyde or ketone at a temperature of from 25°C to 50°C under reaction conditions sufficient to convert the aminoalkanethiol moieties to thiazolidine moieties.
6. The process of Claim 5 characterized in that the ketone is acetone.

#### Patentansprüche

1. Verfahren zum Herstellen eines unlöslichen, stark sauren Kationenaustauscherharzes in saurer Form, modifiziert durch teilweises Neutralisieren seiner Kationenaustauscherkapazität mit einem Aminoalkanthiol, gekennzeichnet durch Inberührungbringen des Kationenaustauscherharzes mit einem N-(2-Mercaptoalkyl)amid in Gegenwart von Wasser bei einer Temperatur

von 80°C-110°C unter zum Ausbilden des modifizierten Kationenaustauscherharzes ausreichenden Reaktionsbedingungen.

2. Verfahren nach Anspruch 1, gekennzeichnet durch Verwenden eines N-(2-Mercaptoalkyl)amids der Formel



in der R, R<sub>a</sub>, R<sub>b</sub>, R<sub>d</sub> und R<sub>e</sub> unabhängig Wasserstoff, Alkyl oder Aryl sind.

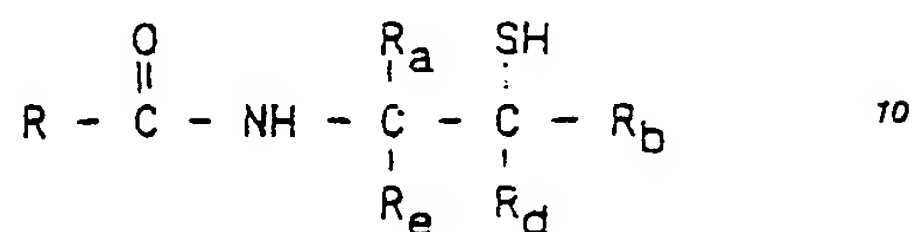
3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß R eine Alkylgruppe mit 1-4 Kohlenstoffatomen ist.
4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß R Methyl oder Ethyl ist und R<sub>a</sub>, R<sub>b</sub>, R<sub>d</sub> und R<sub>e</sub> Wasserstoff sind.
5. Verfahren nach Anspruch 1, gekennzeichnet durch den zusätzlichen Schritt des Inberührungbringens des teilweise neutralisierten Harzes mit einem Aldehyd oder Keton bei einer Temperatur von 25°C-50°C unter zum Umwandeln der Aminoalkanthiolgruppen in Thiazolidingruppen ausreichenden Reaktionsbedingungen.
6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß das Keton Aceton ist.

#### Revendications

1. Procédé de préparation d'une résine échangeuse de cations fortement acide, insoluble, sous forme acide, modifiée par la neutralisation partielle de sa capacité d'échange de cations avec un aminoalkanethiol, caractérisé par la mise en contact de la résine échangeuse de cations avec un N-(2-mercaptoalkyl)amide en présence d'eau à une température de 80°C à 110°C dans des conditions réactionnelles suf-

fisantes pour produire la résine échangeuse de cations modifiée.

2. Procédé selon la revendication 1, caractérisé par l'emploi d'un N-(2-mercaptoalkyl)amide ayant la formule: 5



dans laquelle R, R<sub>a</sub>, R<sub>b</sub>, R<sub>d</sub>, et R<sub>e</sub> sont indépendamment H, un radical ---- alkyle ou aryle. 15

3. Procédé selon la revendication 2, caractérisé en ce que R est un radical alkyle ayant de 1 à 4 atomes de carbone. 20
4. Procédé selon la revendication 3, caractérisé en ce que R est un radical méthyle ou éthyle, et R<sub>a</sub>, R<sub>b</sub>, R<sub>d</sub>, et R<sub>e</sub> sont H. 25
5. Procédé selon la revendication 1, caractérisé par l'étape supplémentaire de mise en contact de la résine partiellement neutralisée avec un aldéhyde ou une cétone à une température de 25 ° C à 50 ° C dans des conditions réactionnelles suffisantes pour convertir les groupes aminoalcanethiol en groupes thiazolidine. 30
6. Procédé selon la revendication 5, caractérisé en ce que la cétone est l'acétone. 35

40

45

50

55